



TITLE:

Engineering the band gap of SiC nanotubes with a transverse electric field

AUTHOR(S):

Alfieri, Giovanni; Kimoto, T.

CITATION:

Alfieri, Giovanni ...[et al]. Engineering the band gap of SiC nanotubes with a transverse electric field. Applied Physics Letters 2010, 97(4): 043108.

ISSUE DATE:

2010-07-26

URL:

<http://hdl.handle.net/2433/126719>

RIGHT:

© 2010 American Institute of Physics

Engineering the band gap of SiC nanotubes with a transverse electric field

G. Alfieri^{1,a)} and T. Kimoto^{1,2}

¹Department of Electronic Science and Engineering, Kyoto University, Kyotodaigaku-katsura, Nishikyo, Kyoto 615-8510, Japan

²Photonics and Electronics Science and Engineering Center, Kyoto University, Kyotodaigaku-katsura, Nishikyo, Kyoto 615-8510, Japan

(Received 15 April 2010; accepted 7 July 2010; published online 28 July 2010)

The effects of a transverse electric field, of intensities ranging from 0 to 0.20 V/Å, on the band gap width of SiC nanotubes (SiCNTs) are investigated by means of density functional theory. A decrease in the band gap width, as a function of the electric field, is observed and the mechanism for such reduction, as well as its dependence on the nanotube diameter, is analyzed. An empirical model to describe the field dependence of the band gap is also proposed. © 2010 American Institute of Physics. [doi:10.1063/1.3469944]

Field emission or the emission of electrons into vacuum due to the quantum tunneling effect under high electric field, has been exploited for a number of applications. As it was found that the tubular phase of carbon has all the desirable electronic and structural properties for being an excellent field emitter,¹ microwave devices for spacecraft and satellite communications,² and flat panel displays³ are strongly benefiting from the use of carbon nanotubes (CNTs).

At the same time, due to the rapid development of present-day technology, there is a strong need of a material whose performance does not degrade when operating in harsh conditions, e.g., at high temperatures or when subject to the bombardment of energetic particles and, for this reason, silicon carbide (SiC) is the prime choice candidate as a replacement of Si for the manufacture of electronics working in hostile environments.⁴

The high energy difference between the sp^2 and sp^3 bonds (1.25 eV per Si–C pair⁵), which makes the existence of a SiC graphitic phase impossible, has not hindered scientist from synthesizing SiC nanotubes (SiCNTs) (Ref. 6) so to make of SiCNTs a possible alternative to CNTs for field emitting applications. This has boosted the interest for SiCNTs in the recent years and several studies on the electronic properties of SiCNTs can be found in the literature.^{7–11}

It is known that SiCNTs are generally semiconductors, except for the (3,0) and (4,0) nanotubes which are metals,⁷ and the band gap (E_g) is wider for larger tube diameters.⁸ Armchair and chiral SiCNTs are indirect semiconductors while zig-zag are direct semiconductors.^{8,9} However, while it was demonstrated that, analogously to CNTs,^{12–14} an applied uniaxial strain results in the modification of both E_g width and band structure of SiCNTs,¹⁰ the effects of an applied electric field on the electronic properties of SiCNTs are still an open question.

A transverse electric field \mathbf{F}_\perp (perpendicular to the nanotube axis) reduces the E_g of a boron nitride NT (BNNT) and this reduction is dependent on the diameter.¹⁵ The \mathbf{F}_\perp sensitivity of a nanotube was attributed to the bond ionicity but no explanation was put forward on its diameter dependence. As it is known that in SiC, C is more electronegative than Si, the questions that arise are: is the E_g of SiCNT sensitive to an

applied \mathbf{F}_\perp ? Does such modification also depend on the diameter of the SiCNT?

In order to answer these questions, we examined the band structure and E_g of five SiCNTs (two armchair and three zig-zag), as a function of \mathbf{F}_\perp of intensities ranging from 0 to 0.20 V/Å, by the *ab initio* calculations code SIESTA.¹⁶ The effect of core electrons was taken into account by employing Troullier–Martins norm-conserving pseudopotentials¹⁷ and the Perdew–Burke–Ernzerhof¹⁸ form of the generalized-gradient approximation (GGA) was used for the exchange correlation potential. A double- ζ plus polarization was used as atomic orbitals basis set throughout the calculations. The SiCNTs employed in this study have 72 [for the (18,0) SiCNT] or 64 atoms which, except for the (8,0) and (8,8) SiCNTs, correspond to the total number of atoms in the unit cell. A layer of approximately 15–20 Å vacuum in the lateral directions was used to avoid artificial tube-tube interactions. The equilibrium configurations of the SiCNTs were obtained by relaxing the atomic coordinates with a conjugate gradient algorithm, until the maximum atomic forces were less than 0.025 eV/Å and the stress tensor less than 0.5 GPa. To speed up the calculations we used a 0.02 Ry energy shift to compress the basis set. The charge density was projected onto a real space grid with an equivalent cutoff of 90 Ry and 8 Monkhorst–Pack special k -points¹⁹ along the nanotube axis ensured the convergence of the calculations. For the unit cells of both armchair and zig-zag SiCNTs we observed an increase in E_g of less than 0.01 eV by either rising the cutoff to 180 Ry or to increase the k -points to 32. By decreasing the energy shift value from 0.02 to 0.01 Ry, an increase in E_g of 0.01 eV and less than 0.02 eV for the unit cells of armchair and zig-zag SiCNTs, respectively, was observed.

In Table I, details of the examined SiCNTs (diameter, number of atoms, and E_g) are presented. It can be seen that the values of E_g are in good agreement with those of Wu *et al.*⁷ and, accordingly to previous reports, smaller diameter SiCNTs have smaller E_g because of σ – π orbitals rehybridization due to the higher curvature.⁸

In Fig. 1, the band structure of the (8,0) and (8,8) SiCNTs for \mathbf{F}_\perp of 0 and 0.20 V/Å are presented. Zig-zag SiCNTs are direct semiconductors at the Γ point [Figs. 1(a) and 1(b)] and the application of \mathbf{F}_\perp has only a weak effect on E_g [Fig. 1(b)] as the estimated E_g reduction is about less than 1% of the zero field value [Fig. 1(b)].

^{a)}Electronic mail: giovanni@semicon.kuee.kyoto-u.ac.jp.

TABLE I. Chirality, diameter, number of atoms employed in the calculations, energy band gap, and type (in parenthesis, d:direct, i:indirect) for the five studied SiCNTs.

| Chirality | Diameter (Å) | Number of atoms | E_g (eV) |
|-----------|--------------|-----------------|------------|
| (8,0) | 7.88 | 64 | 1.17 (d) |
| (8,8) | 13.62 | 64 | 2.17 (i) |
| (16,0) | 15.72 | 64 | 2.02 (i) |
| (18,0) | 17.68 | 72 | 2.08 (d) |
| (16,16) | 27.20 | 64 | 2.38 (i) |

Armchair SiCNTs are indirect semiconductors with a minimum of the conduction band (E_C) at X and a maximum of the valence band (E_V) on the Γ - X direction. However, in the case of the (8,8) SiCNTs supercell [Figs. 1(c) and 1(d)] the X point is projected on the Γ point of the first Brillouin zone. The application of \mathbf{F}_\perp results in the reduction in the E_g [Fig. 1(b)] of about 25% of the zero field value E_{g0} . In order to explain the mechanism for E_g reduction, the behavior of the molecular orbitals under \mathbf{F}_\perp of intensities 0 and 0.20 V/Å, is analyzed.

In Fig. 2 the lowest unoccupied and highest occupied molecular orbitals (LUMO and HOMO, respectively) for the (8,0) SiCNT, are shown. For the 0 V/Å electric field, the LUMO [Fig. 2(a)] and HOMO [Fig. 2(b)] are uniformly distributed along the nanotube. Due to the higher electronegativity of C atoms, the HOMO are localized around the C atoms (in black) while the LUMO is localized around the Si atoms (gray). The presence of \mathbf{F}_\perp induces the formation of an electric dipole moment \mathbf{p} , that means redistribution of both LUMO [Fig. 2(c)] and HOMO [Fig. 2(d)] along the direction of \mathbf{F}_\perp (visualized with a black arrow). The LUMO (positive charges) are for the most part localized on the lower side of the tube, while the HOMO (negative charges), on the upper side.

In Fig. 3, the LUMO and HOMO for the (8,8) SiCNT are displayed. The presence of \mathbf{F}_\perp results in the formation of a dipole with the redistribution of the LUMO and HOMO along the direction of the electric field and such orbital redistribution is more distinct than for the case of the (8,0) SiCNT.

As the \mathbf{F}_\perp induces the formation of an electric dipole, one region of high electrostatic potential [Figs. 2(c) and 3(c)]

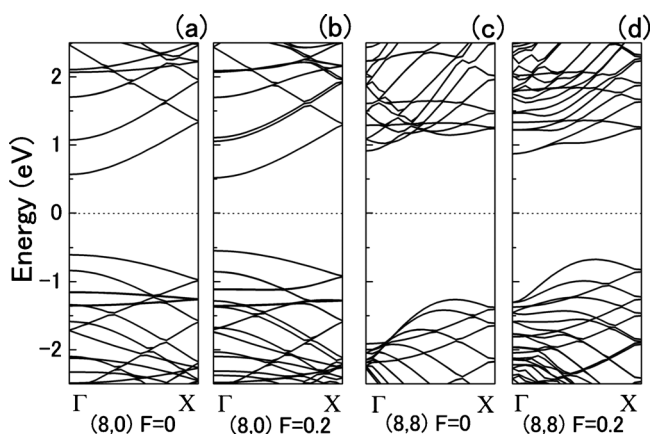


FIG. 1. Band structure of the (8,0) SiCNT for (a) 0 and (b) 0.20 V/Å and of (8,8) SiCNT for (c) 0 and (d) 0.20 V/Å electric field.

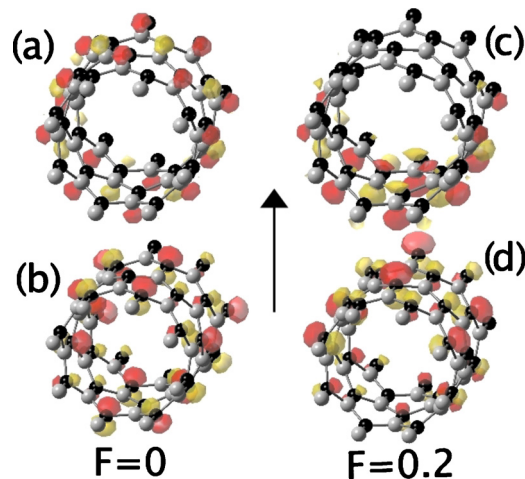


FIG. 2. (Color online) Behavior of the (a) and (c) lowest unoccupied and (b) and (d) highest occupied molecular orbitals under 0 V/Å and 0.20 V/Å electric field, respectively, for the (8,0) SiCNT (isovalue 0.07 $e^-/\text{\AA}^3$). Si atoms are gray and C atoms are black. The arrow indicates the direction of the electric field. Yellow and red are the colors of the positive and negative lobes of the wave function.

and one region of low electrostatic potential [Figs. 2(d) and 3(d)] are formed. From an energy point of view, this means a decrease in the energy of the LUMO and an increase in that of the HOMO, which causes the narrowing of E_g . Yet, for the case of the (8,0) SiCNT, shown in Fig. 2, hints of the HOMO can still be seen in the lower part of the tube and in addition, a region where both LUMO and HOMO coexist can be also seen halfway along the direction of \mathbf{F}_\perp . These two factors combined, prevent the E_g from decreasing any further¹¹ thus explaining why the E_g of the (8,0) SiCNT is less sensitive to an electric field than that of the (8,8) SiCNT, for which the two regions are more distinctly separated.

Figure 4 shows the behavior of E_g as a function of \mathbf{F}_\perp for the SiCNTs investigated in this study. It can be seen that SiCNTs with roughly the same diameter [(16,0) and (18,0) nanotubes or (8,8) and (16,0) nanotubes] display the same behavior under \mathbf{F}_\perp and the larger the diameter, the more sensitive the SiCNTs are to \mathbf{F}_\perp . In order to explain the reason for the diameter dependence, we can invoke the definition of \mathbf{p} which is known to affect the values of E_g , as follows:¹¹

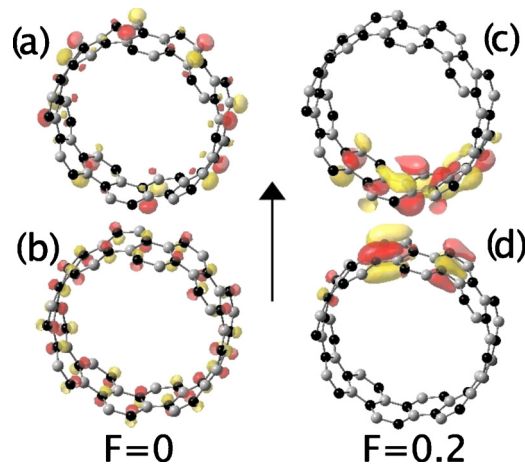


FIG. 3. (Color online) Behavior of the (a) and (c) lowest unoccupied and (b) and (d) highest occupied molecular orbitals under 0 V/Å and 0.20 V/Å electric field, respectively, for the (8,8) SiCNT (isovalue 0.07 $e^-/\text{\AA}^3$).

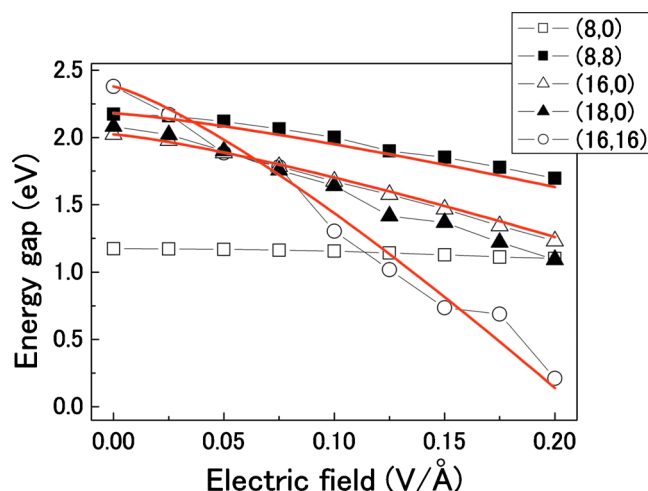


FIG. 4. (Color online) Electric field dependence of the band gap for the six SiCNTs examined in this study. The red solid lines represent the fit for the (8,8), (16,16), and (16,0) SiCNTs as from Eq. (2).

$$\mathbf{p} = \mathbf{p}_0 + \alpha \mathbf{F}, \quad (1)$$

where \mathbf{p}_0 is the spontaneous dipole moment and α is the electric polarizability which, for a homogeneous electric field can be defined as $-\partial^2 U / \partial F^2|_{F=0}$,²⁰ where U is the total energy of the SiCNT. If we consider a fixed value of \mathbf{F}_\perp then, an increase in the value of α , would correspond to higher values of \mathbf{p} , meaning that α is responsible for the E_g reduction. In fact, Wu *et al.*⁷ reported that α is directly proportional to the diameter of SiCNT and since higher values of \mathbf{p} mean lower E_g , the larger the diameter the smaller E_g becomes.

Based on the dependence of the E_g reduction on α (or the diameter), we found that the behavior of E_g versus \mathbf{F}_\perp can be described by a $y=a+b \times x^c$ function, by setting a as the E_g at zero field (E_{g0}), b as a free parameter and $c=5/4$. In order to introduce the diameter D dependence, we fitted the values of b (for each of the studied SiCNTs) versus D , obtaining $B=3.4-0.36 \times D-0.014 \times D^2$. We thus derived the following equation:

$$E_g = E_{g0} + B \times |\mathbf{F}_\perp|^{5/4}, \quad (2)$$

which describes the E_g reduction as a function of \mathbf{F}_\perp for a chosen SiCNT (by setting E_{g0} and D).

We fitted the electric field dependence of the band gap for (8,8), (16,0), and (16,16) SiCNTs according to Eq. (2) (red solid lines) and, as it can be seen, our model describes

quite well the behavior of the three SiCNTs. To further confirm the validity of the proposed model, we applied it to the case of the (13,0) SiCNT. By setting $D=12.8 \text{ \AA}$ and $E_{g0}=1.85 \text{ eV}$, we find that for an electric field of 0.1 and 0.2 V/Å, E_g becomes 1.65 eV and 1.37 eV, respectively, which is in good agreement with the corresponding values found by our *ab initio* calculations (1.66 eV and 1.36 eV for 0.1 V/Å and 0.2 V/Å, respectively).

In summary, the band gap of five SiCNTs was investigated as a function of a transverse electric field. It was found that the induced electric dipole, due to the rearrangement of the molecular orbitals, is responsible for the decrease in the band gap values. The sensitivity of the E_g of SiCNTs to the electric field was explained in terms of electric polarizability, and an analytic function was defined to model the change in band gap as a function of the electric field.

This work was supported by the Japanese Society for the Promotion of Science and by the Global COE Program (C09) from the Ministry of Education, Culture, Sports and Technology, Japan.

- ¹J. M. Bonard, H. Kind, T. Stockli, and L. O. Nilsson, *Solid-State Electron.* **45**, 893 (2001).
- ²K. B. K. Teo, E. Minoux, L. Hudanski, F. Peauger, J. P. Schnell, L. Gangloff, P. Legagneux, D. Dieumegard, G. A. J. Amaratunga, and W. I. Milne, *Nature (London)* **437**, 968 (2005).
- ³M. Mauger and V. T. Binh, *J. Vac. Sci. Technol. B* **24**, 997 (2006).
- ⁴H. Matsunami, *Jpn. J. Appl. Phys.* **43**, 6835 (2004).
- ⁵Y. Miyamoto and B. D. Yu, *Appl. Phys. Lett.* **80**, 586 (2002).
- ⁶T. Taguchi, N. Igawa, H. Yamamoto, S. Shamoto, and S. J. Jitsukawa, *Physica E (Amsterdam)* **28**, 431 (2005).
- ⁷J. J. Wu and G. Y. Guo, *Phys. Rev. B* **76**, 035343 (2007).
- ⁸M. Zhao, Y. Xia, F. Li, R. Q. Zhang, and S. T. Lee, *Phys. Rev. B* **71**, 085312 (2005).
- ⁹A. Gali, *Phys. Rev. B* **73**, 245415 (2006).
- ¹⁰Z. Wang, Z. Zu, H. Xiao, F. Gao, and W. J. Weber, *Appl. Phys. Lett.* **92**, 183116 (2008).
- ¹¹G. Alfieri and T. Kimoto, *Nanotechnology* **20**, 285703 (2009).
- ¹²T. Ito, K. Nishidate, M. Baba, and M. Hasegawa, *Surf. Sci.* **514**, 222 (2002).
- ¹³Y.-R. Chen and C.-I. Weng, *Carbon* **45**, 1636 (2007).
- ¹⁴Y. V. Shtogun and L. M. Woods, *J. Phys. Chem. C* **113**, 4792 (2009).
- ¹⁵C. W. Chen, M. H. Lee, and S. J. Clark, *Nanotechnology* **15**, 1837 (2004).
- ¹⁶J. M. Soler, J. D. Gale, A. Garcia, J. Junquera, P. Ordejon, and D. Sanchez-Portal, *J. Phys. Condens. Matter* **14**, 2745 (2002).
- ¹⁷N. Troullier and J. L. Martins, *Phys. Rev. B* **43**, 1993 (1991).
- ¹⁸J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.* **77**, 3865 (1996).
- ¹⁹H. J. Monkhorst and J. D. Pack, *Phys. Rev. B* **13**, 5188 (1976).
- ²⁰F. Jensen, *Introduction to Computational Chemistry* (Wiley, New York, 2008).